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Distribution, health risk assessment, and water quality criteria of phthalate esters in Poyang Lake, China

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Abstract

Although China has been the main manufacturer and consumer of phthalate esters (PAEs), human health ambient water quality criteria (AWQCs) have not been proposed for these chemicals. In this study, the distribution and bioaccumulation of six PAEs (dimethyl phthalate (DMP), diethyl phthalate (DEP), di-n-butyl phthalate (DBP), butyl benzyl phthalate (BBP), bis (2-ethylhexyl) phthalate (DEHP), and di-n-octyl phthalate (DnOP)) were investigated in 11 edible fish species collected from Poyang Lake, China. The results showed that the total concentrations of the six PAEs in the fish ranged between 118.63 and 819.84 μg/kg wet weight (mean of 327.50 ± 190.44 μg/kg). DMP, DEP, DBP, and DEHP were detected in all samples, of which DEHP and DBP were two of the most predominant phthalates, accounting for more than 90% of the total PAEs. The DEHP concentrations in fish with different habitat preferences were different, demersal species were significantly higher than pelagic species ($p < 0.05$). The mean natural logarithmic bioaccumulation factors (log BAFs) of PAEs increased with increasing lipophilicity of the substances, which yielded the following regression equation: log BAF (L/kg) = 0.103 log K_{ow} + 2.158 ($r^2 = 0.940$, $p < 0.05$, $n = 4$). Using this quantitative structure–activity relationship to calculate BAFs for the remaining undetected substances (BBP and DnOP) to derive AWQCs. According to the natural parameters, the human health AWQCs relating to PAE concentrations for water and fish consumption were derived as 9.4×10^3 (DMP), 5.0×10^2 (DEP), 4.2×10^1 (DBP), 1.1 (BBP), 8.6×10^{-2} (DEHP), and 2.0 (DnOP) μg/L. Human health risk assessment indicated that the dietary intake of DEHP may exert a carcinogenic effect on residents of the Poyang Lake region. The results provide important input to assess the health risk posed by PAEs contaminated surface water.

Keywords Phthalate esters, Aquatic bioaccumulation, Water quality criteria, Human health risk

Introduction

Phthalate esters (PAEs) are a group of chemical plasticizers widely used in polyvinyl chloride production. As they satisfy a broad range of processing and performance requirements, they have many applications, including use in food packaging, medical instruments, electric cables, buildings, and construction [12]. With large-scale production and usage, PAEs accounted for approximately 55% of the global consumption of plasticizers in 2020 [17]. China has the largest plasticizer market globally, accounting for over half of the world's plasticizer consumption in 2020 [17]. Bis (2-ethylhexyl) phthalate (DEHP) and di-n-butyl phthalate (DBP) are two of the

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most abundantly produced phthalates, accounting for more than 80% of the phthalates produced in China [11].

Because PAEs do not chemically bond to products, they escape to the environment easily during production and usage. Therefore, PAEs continue to be detected in various environmental media, including in sediment [22], the atmosphere [9], soil [39], and aquatic ecosystems [23, 28]. In addition, recent studies have indicated that surface waters in China show widespread PAE contamination [10, 42]. In the aquatic environment, these pollutants lead to adverse effects on organisms and threatened human health through bioaccumulation in edible fish [14]. Fish represent a good source of protein, and are consumed in many regions, they also serve as a bio-indicator for assessing the impact of contaminants on human health [4]. In the Pearl River Delta and Yangtze River Delta of China, fish is one of the main food sources for residents [3, 5]. Therefore, data on the presence and distribution of PAEs in fish are important from a human health perspective.

Since DEHP was first detected in the tissues of patients who had received blood transfusions [18], increasing evidence of the direct and indirect health threats that these esters present to humans have been reported [6, 30]. In addition, the International Agency for Research on Cancer has classified butyl benzyl phthalate (BBP) and DEHP as probably and possibly carcinogenic to humans, respectively. The U.S. Environmental Protection Agency (USEPA) listed dimethyl phthalate (DMP), diethyl phthalate (DEP), DBP, BBP, DEHP, and di-n-octyl phthalate (DnOP) as priority environmental pollutants and developed their ambient water quality criteria (AWQCs) to prevent health hazards associated with the consumption of contaminated fish and water. However, human health AWQCs vary from region to region owing to the variation of species. The human health AWQCs of priority PAEs in China have thus far not been reported. Deriving the AWQCs values of these chemicals is critical for establishing safe limits and managing their use and release into the environment.

Poyang Lake is the largest freshwater lake and inland fishery base in China. The PAE concentrations in the water from this region were recently reported by Ai et al. [1], in which the need to protect aquatic organisms from the effects of DEHP was highlighted. However, studies on the distribution and accumulation of PAEs in fish and the associated effects on human health are scarce. Therefore, the primary objectives of this study were to (1) analyze the distribution and bioaccumulation of PAEs in fish; (2) derive the human health AWQCs of PAEs based on natural parameters, and (3) assess health risks based on oral exposure to PAEs from fish and water.

Materials and methods

Study areas

Poyang Lake (28°22′ to 29°45′ N, 115°47′ to 116°45′ E) is located in the north of Jiangxi Province, on the south bank of the middle and lower reaches of the Yangtze River. The area of the lake varies with different seasons, which can reach more than 3000 km^2 during the wet season and drop below 1000 km^2 during the dry season. Poyang Lake collects inflows from five major tributaries (Gan River, Xin River, Rao River, Xiu River, Fu River) and subsequently afflux into the Yangtze River from south to north at Hukou. Poyang Lake is generally composed of north and south parts: the north part is a narrow channel to Yangtze River, and the south part is the main lake. The samples in this study were collected from Hukou (in the north part) and Nanji (in the south part). Hukou is the only entrance to the Yangtze River and the only channel through which fish can migrate between the river and the lake, playing an important role in maintaining the fish resources in Poyang Lake. Nanji is the national wetland nature reserve of Poyang Lake, which plays an important role in the maintenance of diversity and conservation of birds, especially endangered waterbirds. A previous study indicated that DEHP posed an ecological risk in Poyang Lake [1].

Sample collection

The study area and sampling sites are shown in Fig. 1. A total of 121 edible fish were collected from two sites (Hukou and Nanji) in Poyang Lake in July 2019. These biotic samples included 11 species of edible fish commonly consumed in the region [grass carp ($n=8$), crucian ($n=8$), silver carp ($n=8$), bighead carp ($n=10$), and sharpbelly ($n=38$); banded catfish ($n=6$); catfish ($n=13$); Chinese perch ($n=9$); carp ($n=8$); snakehead ($n=4$); and topmouth culter ($n=9$)]. All fish samples were captured by fishing nets on boats and then wrapped in aluminum foil. Information regarding the organisms, such as their scientific name, habitat preference, length, weight, and water content, are listed in Additional file 1: Table S1. A total of 14 water samples from the two sites (Hukou and Nanji) were collected in the dry (December 2018) and wet (July 2019) seasons. Two liters of water from each site (0–0.5 m in depth) were collected with a steel sampler and stored in clean brown glass bottles. The water was then filtered through glass fiber filters (pore diameter 0.7 μm, Whatman, England) that had been baked at 450 °C for 4 h. The biota and water samples were stored at − 20 °C and 4 °C, respectively, until preparation.

Sample preparation

The following six priority PAEs were investigated in this study: DMP, DEP, DBP, BBP, DEHP, and DnOP. A total of

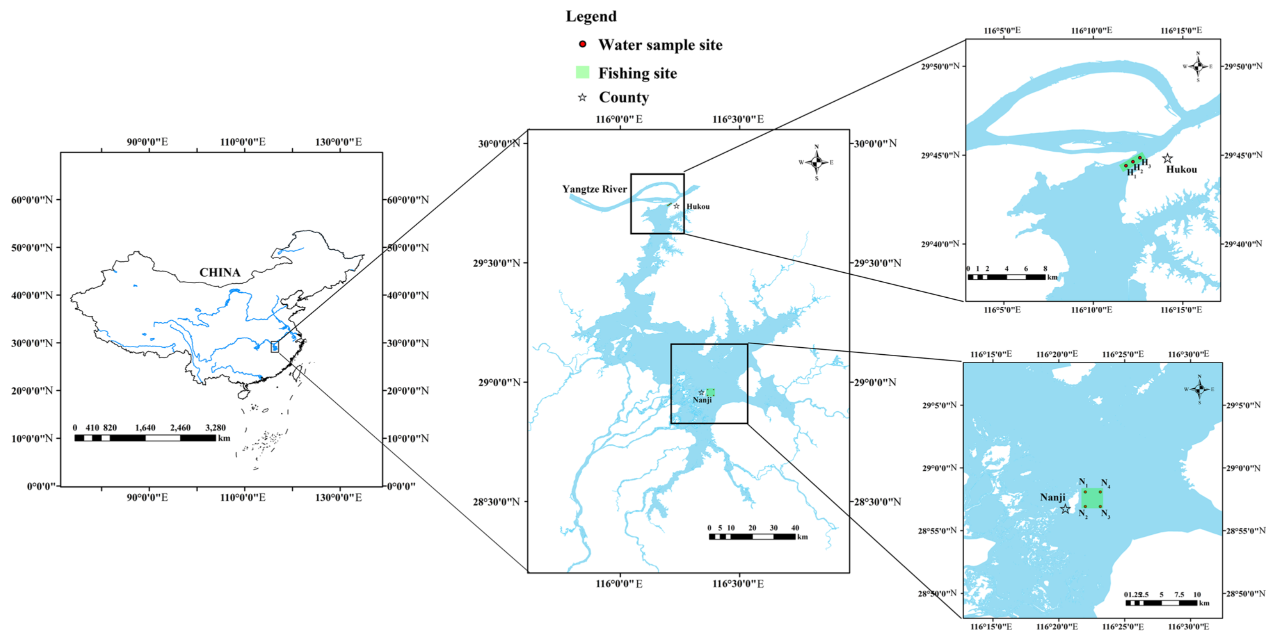

Fig. 1 Map of the study area and location of the sampling sites

1.5–2.0 g of freeze-dried fish muscle samples were accurately weighed out. The samples were then homogenized into a fine powder. The powdered samples were then mixed and equilibrated with 500 ng surrogate standard substance (DEHP-d4) (used to monitor the extraction efficiency of the method) and preconditioned quartz sand (prebaked at 450 °C for 4 h) before accelerated solvent extraction. The samples were extracted with a 60 ml mixture of n-hexane, acetone, and dichloromethane (1:1:1, v/v/v) [5]. A PSA/silica cartridge (6 cc, 500 mg/500 mg, Simply, China) was used to clean the extracting solution owing to its complex composition. Prior to cleaning, the cartridge was conditioned in sequence with 5 mL dichloromethane and 5 mL acetonitrile at a flow rate of 1 mL/min. The extracts were loaded onto preconditioned PSA/silica cartridges at a flow rate of 1 mL/min and collected. Finally, the cartridges were washed twice with 5 mL ultrapure filtered water, and the PAEs were eluted three times with 5 mL acetonitrile at 1 mL/min and then mixed with 1 mL acetone. The mixture of extracts and eluent was reduced under a gentle nitrogen flow at 40 °C and recombined in 1 mL n-hexane with 500 ng internal standard substance (DBP-d4) for analysis by GC/MS. The preparation of water samples was shown in the Additional file, which was the same as the method described in the previous study [1].

The concentrations of PAEs were analyzed using Agilent 7890 gas chromatograph (GC) equipped with an HP-5MS column (30 m × 0.250 mm, 0.25 μm film thickness) coupled with a 5977-mass selective detector (MSD) (Agilent Technologies, CA, USA). The detailed conditions of the GC–MS analysis are discussed in the Additional file.

Quality assurance and quality control

To avoid contamination of PAEs, the use of plastic equipment was avoided in the process of sample collection and preparation, the experimental tools were rinsed with acetone at least two times prior to use, and the quartz sand and filters were baked at 450 °C for 4 h before use. Three solvent blanks were run for every 10 samples, and procedural blanks were prepared to check for background contamination during the injection and pretreatment. The values of procedural blanks were lower than the limit of quantification (LOQ). The correlation coefficients (R^2) of the standard curve derived from seven points (0.02, 0.05, 0.1, 0.2, 0.5, 1.0, and 2.0 mg/L) were greater than 0.995 and the relative standard deviations were less than 10%. The limit of detection (LOD) and LOQ was determined using the following equations:

$$\mathrm{LOD} = 3.3\sigma/S, \tag{1}$$

$$\mathrm{LOQ} = 10\sigma/S, \tag{2}$$

where σ is the standard deviation of the responses, and S is the slope of the calibration curve. The LOQ for the six PAEs ranged between 0.009 and 0.078 μg/L for water samples and 0.096 and 0.198 μg/kg dry weight (dw) for fish samples (Additional file 1: Table S2). The recoveries of the six PAEs ranged between 82 and 113% in water samples and 78 and 127% in fish samples. The recoveries of the surrogate standard (DEHP-d4) ranged from 79 to 91% in water and 75 to 109% in fish. Additionally, the concentrations of the samples less than the LOQ were set as zero [21].

Data processing and analysis

Statistical analysis

The units of PAEs concentration for fish samples were reported as milligram per kilogram wet weight (μg/kg, ww). The significant differences were analyzed with T-test or Mann–Whitney U test. The correlations between the two variables were tested by Pearson correlation analysis and linear regression.

Bioaccumulation factor (BAF)

The BAF is defined as the ratio of the concentration of a chemical in an organism to its concentration in water, which was calculated according to the following equation [38]:

$$\mathrm{BAF} = \mathrm{C_{biota}}/\mathrm{C_{water}}, \tag{3}$$

where C_{biota} is the concentration of PAEs in the biota (μg/kg ww) and C_{water} is the PAEs concentration in water (μg/L).

Trophic level (TL) determination

A stable nitrogen isotope ($\delta^{15}N$) is often used to determine the TL because it shows stable accumulation through food webs. The TLs of aquatic organisms were determined based on the results of δ^{15} N evaluation (Additional file 1: Table S1) according to the following equation [29, 37]:

$$\mathrm{TL_{consumer}} = 2 + \left(\delta^{15}\mathrm{N_{consumer}} - \delta^{15}\mathrm{N_{plankton}}\right)/3.4, \tag{4}$$

where $\delta^{15}N_{consumer}$ and $\delta^{15}N_{plankton}$ are the values of $\delta^{15}N$ for fish and plankton, respectively, number 2 is the TL of plankton, and number 3.4 is the isotopic enrichment factor. $\delta^{15}N$ was analyzed by Elementar Vario (vario PYRO cube, Elementar UK Ltd) coupled with an IsoPrime (100 IRMS, Elementar UK Ltd). A standard sample ($\delta^{15}N = 6.9 \pm 0.2‰$) was inserted for every 12 samples to monitor stability. The detailed analysis procedures are described in the Additional file.

Derivation of human health water quality criteria

The AWQC of PAEs was calculated according to the following equations [32]:

For consumption of water and organisms

$$\mathrm{AWQC} = \frac{\text{toxicity value} \times \mathrm{BW}}{\mathrm{DI} + \sum_{i=2}^{4}\left(\mathrm{FCR}_i \times \mathrm{BAF}_i\right)}. \tag{5}$$

For consumption of organisms only

$$\mathrm{AWQC} = \frac{\text{toxicity value} \times \mathrm{BW}}{\sum_{i=2}^{4}\left(\mathrm{FCR}_i \times \mathrm{BAF}_i\right)}, \tag{6}$$

where toxicity value is the reference dose (RfD) × the relative source contribution (RSC) for non-carcinogenic effects or 10^{-6}/cancer slope factor (CSF) for carcinogenic effects. BW is the body weight of inhabitants; DI is the drinking water intake for natives; and FCR_i and BAF_i are the fish consumption rate and BAF for aquatic TLs 2, 3, and 4, respectively.

Health risk assessment

The hazard quotient (HQ) was developed by the United States Environmental Protection Agency [31] and used to assess the risk. Two methods were used to calculate HQ in this study, one of which is the ratio of the concentration of chemicals in water and the AWQC values (Eq. 7). Another method was generally used in previous studies, which was calculated as the ratio of the estimated daily intake (EDI) and the RfD of PAEs (Eqs. (8, 9, 10)) [2, 41]. Generally, while HQ values less than 1 were considered to indicate negligible adverse health effects as a result of exposure [13]:

$$\mathrm{HQ} = \frac{\mathrm{C_w}}{\mathrm{AWQC}}, \tag{7}$$

$$\mathrm{EDI}_{fish} = \frac{\mathrm{IR}_f \times \mathrm{C}_f}{\mathrm{BW}}, \tag{8}$$

$$\mathrm{EDI}_{water} = \frac{\mathrm{IR}_w \times \mathrm{C}_w}{\mathrm{BW}}, \tag{9}$$

$$\mathrm{HQ} = \frac{\mathrm{EDI}_{fish} + \mathrm{EDI}_{water}}{\mathrm{RfD}}, \tag{10}$$

where EDI_{fish} and EDI_{water} are the average daily intake of PAEs per unit body weight exposure to fish and water, respectively; IR_f is the ingestion rate of fish for natives; IR_w is the ingestion rate of water, similar to the DI in Eq. (5); C_f is the concentration of PAEs in fish (μg/kg ww); and C_w is the concentration of PAEs in water (μg/L).

Table 1 Mean ± standard deviation and range (in parenthesis) of phthalate ester concentrations (μg/kg, ww) in fish according to location and species

Group	Trophic level	Habitat preference	Picture	n	DMP	DEP	DBP	BBP	DEHP	DnOP	∑6PAEs
Location											
Nanji				100	9.17 ± 7.55	6.93 ± 3.20	91.88 ± 37.62	–	138.53 ± 89.98	–	247.37 ± 128.47
					(2.83–40.06)	(3.36–17.80)	(40.45–195.38)	(nd-4.94)	(34.26–401.65)	(nd-9.25)	(118.63–633.81)
Hukou				21	17.77 ± 10.85	10.09 ± 3.27	245.06 ± 75.71	-	280.53 ± 107.24	–	555.23 ± 149.92
					(2.59–39.39)	(4.65–16.46)	(161.18–418.23)	(nd-3.51)	(138.05–468.58)	(nd-5.09)	(354.03–819.86)
Species											
Grass carp	2.09	Pelagic		8	14.78 ± 8.02	7.69 ± 3.78	148.71 ± 99.88	–	100.32 ± 74.39	–	272.70 ± 176.95
					(6.33–30.42)	(5.16–16.46)	(64.08–315.67)	(nd-3.48)	(34.26–229.46)	(nd-4.63)	(129.09–488.84)
Crucian	2.26	Demersal		8	14.58 ± 4.71	11.05 ± 1.93	193.36 ± 97.11	–	226.21 ± 20.58	–	445.40 ± 111.92
					(9.35–24.23)	(7.58–14.06)	(99.42–403.74)	nd	(190.37–252.80)	nd	(354.72–687.38)
Silver carp	2.49	Pelagic		8	5.61 ± 3.56	6.51 ± 2.06	123.14 ± 54.39	–	175.76 ± 131.94	–	312.07 ± 180.23
					(2.59–11.78)	(3.62–9.32)	(78.02–203.21)	(nd-3.51)	(77.19–466.78)	(nd-3.37)	(182.26–684.03)
Bighead carp	2.72	Pelagic		10	9.20 ± 3.74	6.82 ± 2.59	117.12 ± 76.85	–	131.67 ± 125.23	–	265.65 ± 199.40
					(5.53–17.16)	(4.65–12.82)	(57.94–255.30)	nd	(52.64–411.28)	(nd-5.09)	(142.26–656.93)
Sharpbelly	3.07	Pelagic		38	4.49 ± 1.46	12.19 ± 5.89	66.94 ± 14.44	–	100.45 ± 8.70	–	184.28 ± 29.60
					(3.55–6.17)	(6.05–17.80)	(55.34–83.11)	nd	(94.59–110.44)	nd	(161.46–217.73)
Banded catfish	3.31	Demersal		6	29.42 ± 7.14	11.45 ± 3.71	174.90 ± 14.04	–	358.32 ± 32.34	–	572.22 ± 52.70
					(22.99–40.06)	(8.22–17.76)	(160.99–195.38)	nd	(315.76–401.65)	nd	(500.56–634.02)
Catfish	3.81	Demersal		13	9.01 ± 5.91	7.82 ± 2.90	146.53 ± 83.90	–	239.14 ± 110.81	–	404.69 ± 195.01
					(3.17–20.85)	(4.43–12.92)	(73.66–322.51)	(nd-4.49)	(151.64–468.58)	(nd-9.25)	(249.24–819.98)
Chinese perch	3.85	Demersal		9	3.74 ± 0.48	4.71 ± 0.94	67.51 ± 18.57	–	160.97 ± 47.57	–	239.36 ± 51.69
					(2.98–4.31)	(3.36–6.02)	(40.45–81.39)	nd	(102.19–222.98)	(nd-6.90)	(173.82–308.47)
Carp	3.87	Demersal		8	12.93 ± 8.88	7.08 ± 3.88	110.64 ± 72.35	–	131.04 ± 76.73	–	264.04 ± 156.02
					(4.34–31.27)	(3.64–14.81)	(47.43–217.44)	(nd-4.94)	(51.40–266.35)	nd	(118.70–454.67)
Snakehead	3.96	Pelagic, Demersal		4	7.02 ± 1.55	4.67 ± 0.83	75.86 ± 9.53	–	72.48 ± 5.15	–	160.23 ± 8.14
					(5.59–9.11)	(3.56–5.37)	(66.88–86.45)	nd	(65.72–77.98)	nd	(151.51–171.16)

Table 1 (continued)

Group	Trophic level	Habitat preference	Picture	n	DMP	DEP	DBP	BBP	DEHP	DnOP	∑6PAEs
Topmouth culter	4.41	Pelagic		9	15.61 ± 15.55	8.38 ± 2.89	184.33 ± 133.82	–	211.60 ± 143.64	–	421.01 ± 286.74
					(3.52–39.39)	(5.48–12.57)	(70.17–418.23)	nd	(104.76–466.90)	(nd-4.41)	(194.09–826.25)

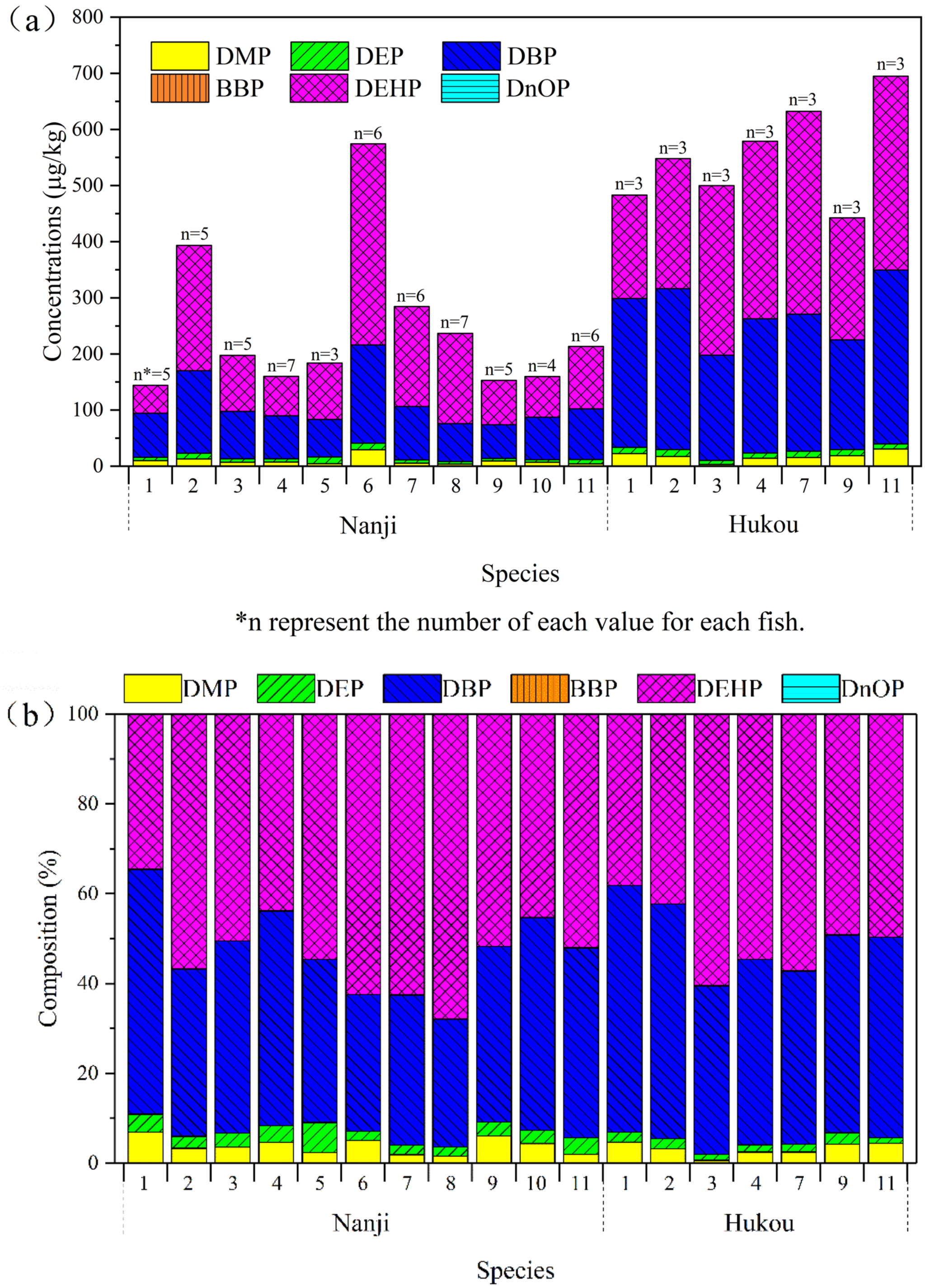

Fig. 2 Concentration (**a**) and composition (**b**) of six phthalate esters in the aquatic organisms in Poyang Lake. In order, the numbers 1 to 11 represent grass carp, crucian, silver carp, bighead carp, sharpbelly, banded catfish, catfish, Chinese perch, carp, snakehead, and topmouth culter

Results and discussion

Occurrence of PAEs in fish

Concentrations of PAEs in fish

A summary of the concentrations of the target PAEs in fish from Poyang Lake is provided in Table 1 and Fig. 2. The detection frequencies (DFs) of the four PAEs (DMP, DEP, DBP, and DEHP) were 100%. Among the target PAEs, BBP (DF 5.8%) and DnOP (DF 8.3%) were detected in only a few samples because their concentrations were found to be extremely low in the aquatic environment of Poyang Lake (Additional file 1: Table S3). The total PAE concentration detected in fish ranged from 118.63 to 819.84 μg/kg and averaged 327.50 ± 190.44 μg/kg. DEHP was the predominant compound (mean 175.49 ± 113.01 μg/kg), followed by DBP (mean 131.75 ± 83.99 μg/kg), accounting for 52.3% and 40.9% of the total PAEs concentration, respectively. As DEHP and DBP are the most extensively produced and used PAE congeners, their dominance in aquatic species has also been observed in other studies [5, 16, 21].

The concentrations of 6 PAEs in water are shown in Additional file 1: Table S3. The results indicated that the total PAEs concentrations in Hukou were significantly higher than that in Nanji (T-test was used for the comparison of mean values, $p < 0.05$). The difference in pollution levels in the two sites resulted in significantly lower concentrations of PAEs in fish from Nanji (247.37 ± 128.47 μg/kg) than that in fish from Hukou (555.23 ± 149.92 μg/kg) (Mann–Whitney U test, $p < 0.001$). The previous study has indicated that the concentrations of PAEs in fish had a positive relationship with the concentrations in water [21]. In addition, the proportion of each compound in the total PAEs did not vary by location (Fig. 2). Compared with another study, the concentrations of PAEs in the present study were much lower than those in freshwater fish from the Hong Kong market (2370 ± 520 μg/kg ww) [5]. The biological data, including the length and weight of the fish, are presented in Additional file 1: Table S1. For each species, there was no significant correlation between length or weight and the total PAE concentrations (Pearson correlation analysis was used, $p > 0.05$) (data not shown).

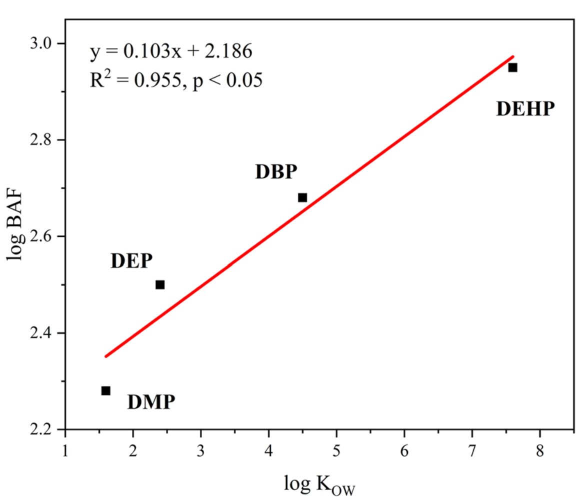

Fig. 3 The relationship between the mean logarithmic bioaccumulation factors (log BAFs) and the octanol–water partition coefficients (log K_{OW}) of the phthalate esters

BAFs of PAEs

Field-measured BAFs for four PAEs (DMP, DEP, DBP, and DEHP) with high DFs in water and fish are presented in Fig. 3, and their concentrations in water are listed in Additional file 1: Table S3. The octanol–water partition coefficient (log K_{ow}) is a primary influence of the BAF of persistent compounds [7]. In the present study, a significantly positive relationship between the log BAF values of PAEs and their log K_{ow} values was observed as log BAF (L/kg) = 0.103 log K_{ow} + 2.158 (Pearson correlation analysis and linear regression were used, $r^2 = 0.940$, $p < 0.05$, $n = 4$). These results verified that PAEs with higher molecular weights can be absorbed by aquatic species more efficiently than those with lower molecular weights. The bioaccumulation levels of DEHP were significantly different in biota with different habitat preferences (Mann–Whitney U test, $p < 0.001$), with greater bioaccumulation in demersal fish than that in pelagic fish. A previous study has reported that DEHP is efficiently adsorbed to sediments because of its high hydrophobicity (log K_{ow} = 7.6) [21]. Demersal fish are constantly exposed to the sedimentary environment, where they ingest contaminated particulate matter, causing a high concentration of DEHP in the fish. Previous studies have demonstrated that the habitat preference of fish and the physicochemical properties of phthalates influence the distribution of PAEs in fish [15, 16].

Bioaccumulation in food webs is not only a lipid–water partitioning process, but can also cause additional bioaccumulation [19]. Previous studies have reported that the BAFs of perfluoroalkyl substances (PFASs) [8], bisphenols (BPs) [38], and polychlorinated biphenyls (PCBs) [37] are positively correlated with trophic levels. In the present study, linear regression analysis showed no statistically significant relationship between BAFs and $\delta^{15}N$ (Fig. 4) (neither for PAEs with lower nor higher molecular weight). This result suggests that the direct exchange and partitioning of these chemicals between the biota and water is an important route of exposure. A previous study reported no statistical correlation between the concentrations of PAEs (i.e., DMP, DEP, di-iso-butyl phthalate (DiBP), DBP, and BBP) and trophic position or $\delta^{15}N$ in marine organisms [24].

Human health AWQCs of PAEs

Using this quantitative structure–activity relationship (log BAF (L/kg) = 0.103 log K_{ow} + 2.158) to calculate BAFs for the remaining undetected substances (BBP and DnOP) (Table 2). Exposure factors required to derive AWQCs for human health are presented in Table 3. AWQCs have been derived to protect human health from the adverse effects of pollutants in contaminated water and fish. However, human exposure to PAEs involves not

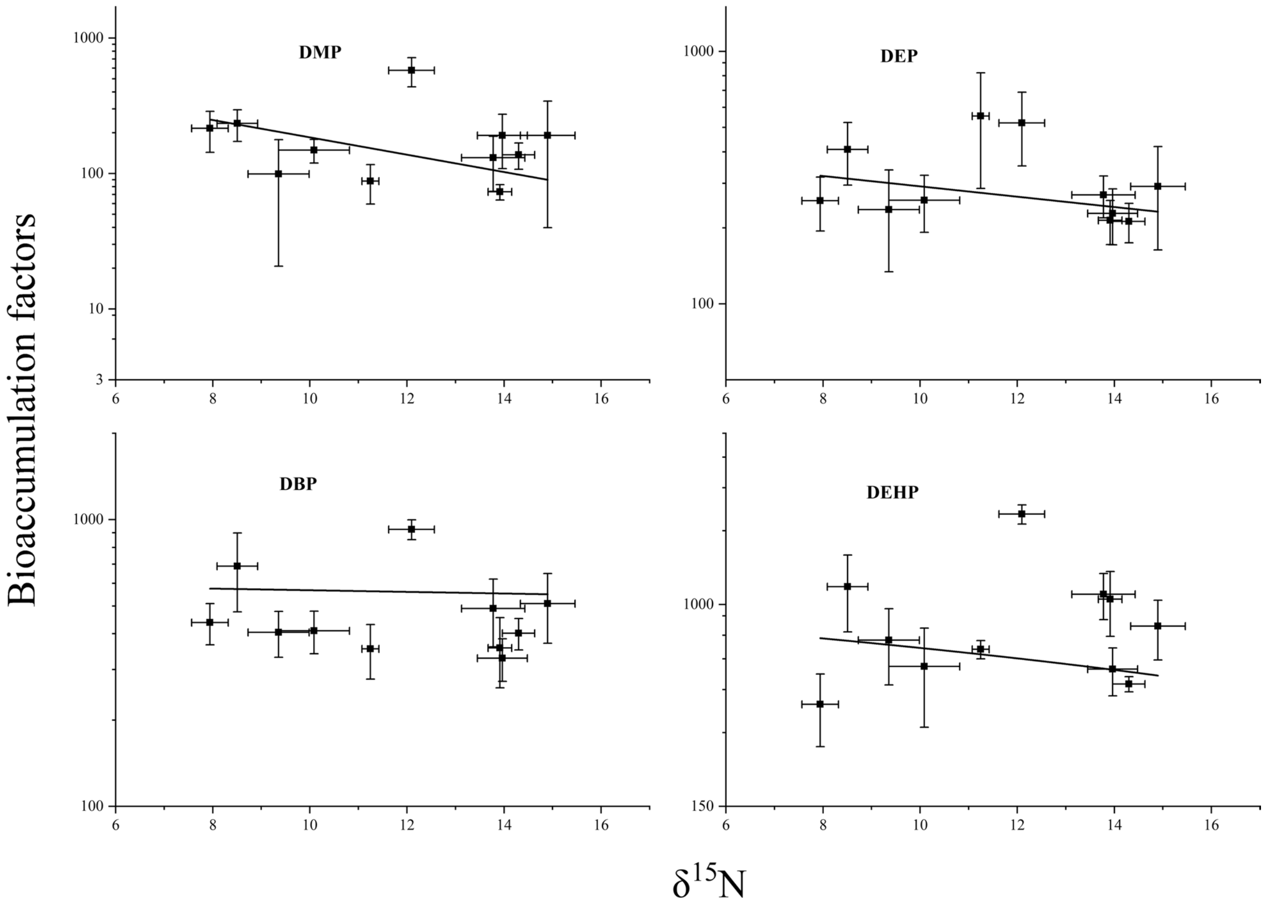

Fig. 4 Bioaccumulation factors of phthalate esters in freshwater fish as a function of $\delta^{15}N$

Table 2 Toxicity parameters, bioaccumulation factors and n-octanol–water partition coefficient (log K_{ow}) for the six PAEs

Chemical	Log K_{ow} [a]	RfD (mg/kg/d)	CSF (per mg/kg/d)	Tested BAF values (L/kg)	Estimated BAF values (L/kg) [d]	Estimated/tested values (%)
DMP	1.60	10[b]	–	190	223	117.4%
DEP	2.42	0.8[b]	–	314	271	86.3%
DBP	4.50	0.1[b]	–	482	448	93.0%
BBP	4.73	1.3[b]	0.0019[b]	–	474	–
DEHP	7.60	0.06[b]	0.014[b]	894	945	105.7%
DnOP	8.10	0.01[c]	–	–	1066	–

[a] Data from the Estimation Programs Interface (EPI) Suite[TM] (https://www.epa.gov)

[b] Data from [33, 36]

[c] Data from [35]

[d] Relationship between log K_{ow} and log BAF for the four substances: log BAF (L/kg) = 0.103 log K_{ow} + 2.186

only fish and water consumption, but also the consumption of fruits, vegetables, meats, and grains; dermal exposure; and inhalation exposure [3]. Therefore, RSC was applied to account for other potential human exposures to the pollutants [32]. Some studies have shown that dietary intake is the dominant exposure route in humans, accounting for over 90% of the total phthalate intake and that aquatic products as food are the main PAE intake

Table 3 Human health ambient water quality criteria and exposure parameters for different populations

Age group	Region	Body weight (kg)	Drinking water intake (L/d)	Fish intake (kg/d)	Consumption type	AWQC (μg/L)					
						DMP	DEP	DBP	BBP	DEHP	DnOP
Adult	Jiangxi Province, China	57.8[a]	2.090[a]	0.0263[a]	Consumption of water and fish	1.6×10^{4}	8.9×10^{2}	7.8×10^{1}	2.1×10^{0} (1.0×10^{3})[d]	1.6×10^{-1} (2.7×10^{1})	3.8×10^{0}
					Consumption of fish	2.3×10^{4}	1.1×10^{3}	9.1×10^{1}	2.4×10^{0} (1.2×10^{3})	1.8×10^{-1} (3.0×10^{1})	4.1×10^{0}
Child (6–8)		26.0[b]	1.228[b]	0.0228[b]	Consumption of water and fish	9.4×10^{3}	5.0×10^{2}	4.2×10^{1}	1.1×10^{0} (5.6×10^{2})	8.6×10^{-2} (1.4×10^{1})	2.0×10^{0}
					Consumption of fish	1.2×10^{4}	5.8×10^{2}	4.7×10^{1}	1.3×10^{0} (6.2×10^{2})	9.1×10^{-2} (1.5×10^{1})	2.1×10^{0}
Child (9–11)		35.0[b]	1.134[b]	0.0198[b]	Consumption of water and fish	1.4×10^{4}	7.6×10^{2}	6.6×10^{1}	1.8×10^{0} (8.6×10^{2})	1.3×10^{-1} (2.2×10^{1})	3.1×10^{0}
					Consumption of fish	1.9×10^{4}	9.0×10^{2}	7.3×10^{1}	2.0×10^{0} (9.7×10^{2})	1.4×10^{-1} (2.4×10^{1})	3.3×10^{0}
Child (12–14)		43.2[b]	1.245[b]	0.0182[b]	Consumption of water and fish	1.8×10^{4}	9.9×10^{2}	8.6×10^{1}	2.3×10^{0} (1.1×10^{3})	1.8×10^{-1} (3.0×10^{1})	4.2×10^{0}
					Consumption of fish	2.5×10^{4}	1.2×10^{3}	9.8×10^{1}	2.6×10^{0} (1.3×10^{3})	1.9×10^{-1} (3.2×10^{1})	4.4×10^{0}
Child (15–17)		51.6[b]	1.244[b]	0.0342[b]	Consumption of water and fish	1.4×10^{4}	7.2×10^{2}	6.1×10^{1}	1.6×10^{0} (8.1×10^{2})	1.2×10^{-1} (2.0×10^{1})	2.9×10^{0}
					Consumption of fish	1.7×10^{4}	8.1×10^{2}	6.6×10^{1}	1.8×10^{0} (8.7×10^{2})	1.3×10^{-1} (2.1×10^{1})	3.0×10^{0}
Adult[c]	USA	80.0	2.4	0.022	Consumption of water and fish	2.0×10^{3}	6.0×10^{2}	2.0×10^{1}	1.0×10^{-1} (4.9×10^{1})	3.2×10^{-1} (5.0×10^{1})	-
					Consumption of fish	2.0×10^{3}	6.0×10^{2}	3.0×10^{1}	1.0×10^{-1} (5.0×10^{1})	3.7×10^{-1} (6.0×10^{1})	-

[a] Data from the Exposure Factors Handbook of the Chinese Population (adults) [25]

[b] Data from the Exposure Factors Handbook of the Chinese Population (children 6–17 years) [26]

[c] Data from Update of human health ambient water quality criteria [36]

[d] Data in parenthesis were the AWQCs based on the noncarcinogenic effects for BBP and DEHP

routes for the Chinese population. [3, 20]. However, detailed information regarding human exposure in the study area is limited. According to the exposure decision tree method mentioned in [32], a recommended RSC value of 20% was assigned in this study.

The results of human health AWQCs for the six PAEs are shown in Table 3, which were different from the USEPA national recommended values because of the difference in exposure factors and BAFs in the two locations. In particular, the variability in the extent of accumulation in aquatic biota between individuals caused a large difference between the values derived in this study and those recommended by the USEPA for DMP. The DI was similar between the two locations, but the average adult BW among the USA population was higher than that of the Chinese population. Assuming that the toxicity value and BAF remained constant, a higher average BW in the AWQC calculation (Equations five and six) resulted in a higher AWQC. Compared with fish consumption, water consumption made a small contribution to phthalate exposure. Moderate to highly hydrophobic chemicals (i.e., log K_{ow} values more than 4.0) have a greater tendency to absorb into organisms [32].

Owing to low bioaccumulation and toxicity, the AWQC values of DMP and DEP were far higher than the surface water concentrations. In addition, the Chinese standard for drinking water dictates that the limit of DEP should be 300 μg/L, which is similar to the human health AWQC [27]. However, the limit value of standards for drinking water quality for DBP in China is 3 μg/L, which is much lower than the calculated AWQC. The national environmental quality standard considers not only the protection of human health, but also the health of aquatic organisms. This may be one of the reasons why the standard of DBP differed by an order of magnitude from the human health AWQC but was in line with the aquatic organisms' AWQC (2.31 μg/L) [1]. DEHP is a possible carcinogenic agent to humans with high rates of bioaccumulation. It had the lowest AWQC at 8.6×10^{-2} μg/L. However, the drinking water quality standard of DEHP of the World Health Organization and China was 8 μg/L, whereas the USEPA's recommended value was 6 μg/L [27, 34, 40]. These standards were between 70 and 90 times higher than the AWQC. DEHP is one of the most abundant phthalates and the most predominant congener in freshwater [11]. Water quality criteria are scientific judgments on the relationship between pollutant concentrations and environmental and human health effects, and water quality standards also need to consider the economic impacts or technological feasibility of meeting pollutant concentrations in ambient water on this basis. This is also the reason for the order-of-magnitude difference between the AWQC and standards for DEHP.

Risk assessment of PAE exposure via water and fish consumption

Our previous study investigated the distribution of six priority PAEs in Poyang Lake, the concentrations of PAEs from 21 sites in Poyang Lake presented in Additional file 1: Table S4 (the average of wet and dry seasons) were used to evaluate health risk [1]. Combining the data of concentrations in water and fish, the EDI via water and fish consumption was calculated based on the national exposure factors of the Chinese residents (Fig. 5). The results showed that the EDI_{water} and EDI_{fish} of the total PAEs ranged from 15.98 to 31.30 and 135.27 to 281.55 ng/kg bw/day, respectively. EDI_{fish} was much higher than EDI_{water} regardless of age group and substance. There is hardly any intake of BBP and DnOP through the consumption of fish and water.

The HQ values derived through two methods are presented in Additional file 1: Table S5. Overall, the HQ values for non-carcinogenic effects of PAEs were much less than 1 (from less than 9.89×10^{-7} to 1.03×10^{-2}). The results indicated that there were no expected adverse effects from these compounds on residents through the consumption of fish and water. Comparing the results of the two methods, the HQ values derived by AWQCs were higher than that derived by EDI. It may be caused by the relative source contribution of 20% for non-carcinogenic effects used in the derivation of AWQC (Additional file 1: Fig. S1)

Moreover, the risk associated with the carcinogenic effect of BBP and DEHP was estimated by the carcinogenic AWQC. BBP was rarely detected in water and fish, the HQ values of BBP were much less than 1, so there was no increased carcinogenic risk posed by BBP. However, the HQ values of DEHP were more than 1 in some age groups (ranging from 0.84 to 1.72), it indicated that the incremental cancer risk exceeds the acceptable recommended value of 10^{-6}. Therefore, the health risk from consumption of water and aquatic product for DEHP in surface water should be concerning.

Conclusions

This study investigated the concentrations and compositions of PAEs in fish from Poyang Lake in China, and human health AWQCs were derived based on natural parameters. All fish in Poyang Lake were polluted with PAEs, with the highest levels occurring in banded catfish. Of the PAEs, DBP and DEHP were most abundant, which is consistent with the results for aquatic environments reported by other countries. The DEHP levels in fish with different habitat preferences revealed spatial differences in PAE concentrations, with greater concentrations in demersal species compared to that in pelagic species. The concentration of PAEs varies

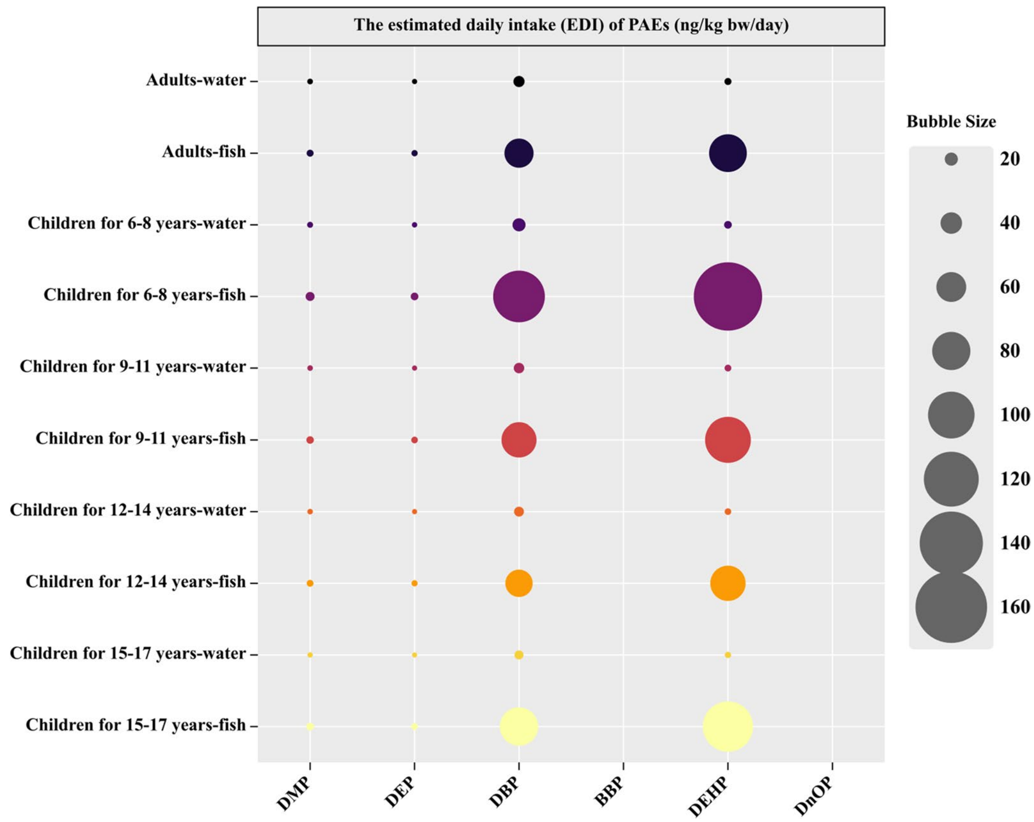

Fig. 5 The estimated daily intake (EDI) of PAEs per unit body weight exposure to fish and water for adults and children

among species but not according to size and tropic level. The human health AWQCs of phthalate were 9.4×10^3 (DMP), 5.0×10^2 (DEP), 4.2×10^1 (DBP), 1.1 (BBP), 8.6×10^{-2} (DEHP), and 2.0 (DnOP) μg/L for the consumption of water and fish and 1.2×10^4 (DMP), 5.8×10^2 (DEP), 4.7×10^1 (DBP), 1.3 (BBP), 9.1×10^{-2} (DEHP), and 2.1 (DnOP) μg/L for fish consumption. The detected residues of DEHP found in the water and fish from Poyang Lake may pose a cancer risk to humans. Therefore, there is a need for further studies on contaminant sources and mitigation measures to achieve a clean environment.

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-022-00702-3.

Additional file 1: **Table S1** Information on the fish samples collected from Poyang Lake. **Table S2** LODs and LOQs for spiked blank samples. **Table S3** The concentrations of PAEs and parameters in water from Nanjishang and Hukou. **Table S4** The concentration of PAEs in water and fish from Poyang Lake. **Table S5** Human health risk assessment of PAEs through drinking water and consuming fish by HQ methods. **Fig. S1** The normal distribution of log BAF for DEHP in pelagic and demersal fish.

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Author contributions

SA: investigation, experiment, formal analysis, methodology, writing—original draft. XW: methodology, writing—review and editing. XG: investigation. QX: experiment. JL: conceptualization, supervision, writing—review and editing. ZL: project administration, funding acquisition. All authors read and approved the final manuscript.

Availability of data and materials

Not applicable.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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